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Oxidative-Alkaline Leaching of Washed 241-SY-102 and 241-SX-101 Tank Sludges and Its Impact on Immobilized High-Level Waste

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Abstract: This report describes work designed to evaluate the effectiveness of alkaline permanganate contacts at selectively removing chromium from the Hanford tank sludges 241-SY-102 and 241-SX-101. The key variables examined in this study, as compared to contact with the standard conditions of stoichiometric permanganate in 3 M hydroxide at elevated temperature, were: a) excess permanganate and hydroxide at elevated temperature, b) sequential elevated temperature 3 M hydroxide leach combined with either a room temperature permanganate contact or an elevated temperature permanganate contact at 0.25 M hydroxide. It was determined that sequential permanganate and caustic leaching can provide as effective removal of Cr as the combined high hydroxide permanganate contact at elevated temperature while minimizing concomitant Pu dissolution.

Keywords: Oxidative leaching, chromium, Hanford tank sludge, permanganate

INTRODUCTION AND BACKGROUND

Currently, there are approximately 200,000 m^3 of radioactive waste in the 177 underground storage tanks located at the U.S. Department of Energy's (DOE's) Hanford Site. As part of the remediation efforts for these underground storage tanks, DOE plans to retrieve, pretreat, immobilize, and dispose of this radioactive waste. This tank waste is generally divided into

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three fractions: supernatant, saltcake, and sludge. The liquid supernatant is alkaline with high concentrations of salts such as sodium nitrate ($NaNO_3$), nitrite ($NaNO_2$), hydroxide (NaOH), carbonate (Na_2CO_3), phosphate (Na_3PO_4), and sulfate (Na_2SO_4). The saltcake is a solid phase consisting primarily of the above-mentioned components as precipitated salts. The sludge portion is a solid phase that consists primarily of precipitated metal oxides/hydroxides. The tank waste contains both mixed-fission products, such as ^{137}Cs, ^{90}Sr, and ^{99}Tc, and actinides, primarily uranium, plutonium, and americium. The actinides and ^{90}Sr are mostly found in the sludge layer while the ^{137}Cs and ^{99}Tc are partitioned amongst all three phases.

The tank wastes will be separated into high-level waste (HLW) and low-activity waste (LAW) fractions. The LAW will be processed to remove most of the dissolved radionuclides, with the remaining material being immobilized in a glass matrix. The HLW will be immobilized in a borosilicate glass and cast into stainless steel canisters. The stainless steel canisters will be ultimately disposed of by placement in a geologic repository (1). Because of the expected high costs associated with HLW immobilization and disposal, pretreatment processes will be performed to reduce the volume of the immobilized HLW (IHLW).

Caustic leaching is the baseline method for pretreating Hanford tank sludges (2). Caustic leaching is expected to remove a large fraction of the aluminum, which is present in large quantities in Hanford tank sludges, by converting poorly soluble aluminum oxides/hydroxides to the more soluble sodium aluminate, $NaAl(OH)_4$. It is also expected that water-insoluble transition metal phosphates and sulfates will metathesize to their water-insoluble transition metal hydroxides and soluble Na_3PO_4 and Na_2SO_4. This will remove significant portions of phosphorus and sulfur, which are poorly tolerated in borosilicate glass, from these HLW solids.

Chromium too can interfere with the HLW immobilization process, in particular by increasing the liquidus temperature (T_L) of spinels ($[Fe,Mn,Ni][Fe,Cr,Mn]_2O_4$), by precipitating as eskolaite (Cr_2O_3), or by promoting molten salt (e.g., mixed alkali-sulfate, -chromate, -phosphate, -molybdate) segregation. For wastes with relatively high concentrations of Fe_2O_3 (>5 mass% in glass) or NiO (>0.5 mass% in glass), spinel precipitation is the most likely result. Spinel precipitation from the HLW glass could short the heating electrodes, clog the pour spout, or otherwise jeopardize the operation and life of the melter (3). Relatively low concentrations of chromium in the HLW can promote spinel formation. Indeed, the chromium concentration in the high-level fraction of Hanford tank waste has the strongest influence on the volume of IHLW to be produced at Hanford (4–6). For these reasons, minimizing the amount of residual chromium in selected Hanford tank sludges is an important pretreatment objective.

Studies on the speciation of chromium in actual Hanford tank sludges have indicated that chromium exists both in its +3 and +6 oxidation states, with the ratio of Cr(VI) to Cr(III) varying greatly, depending on the sludge examined (Table 1). However, the dissolved chromium, regardless of its initial oxidation state in the sludge, was present in caustic-leach solutions (within experimental uncertainty) only in the +6 oxidation state (7–9). Furthermore, although the chromium remaining after caustic leaching is present only in the +3 oxidation state, the fraction of chromium removed often exceeds the amount initially present in the +6 oxidation state. These results imply that chromium initially present in the sludge in the +3 oxidation state underwent oxidation either during or after dissolution. The extent to which the Cr(III) fraction was removed during caustic leaching varied widely from sludge to sludge (Table 1). The observation that chromium present in solution during sludge washing and caustic leaching of Hanford tank wastes exists, within experimental error, in the +6 oxidation state has been supported by a large number of more recent sludge washing and caustic-leaching studies (10–15).

This observation of Cr dissolution occurring only when Cr is present as Cr(VI), regardless of its initial oxidation state, led to the hypothesis that enhancements to ready Cr dissolution could be obtained by contact of the sludges with leach solution containing oxidants. Studies over the last several years with Hanford tank sludge simulants and with actual Hanford tank sludges indicate that treating water-washed and caustic-leached solids with oxidizing agents indeed can significantly increase the effectiveness of chromium removal (16, 19–29). Tested oxidants to date include ozone, O_3 (19, 20, 22), hydrogen peroxide, H_2O_2 (20, 23–26), permanganate, MnO_4^- (16–19, 22, 23, 26–29), oxygen, O_2 (19, 24), persulfate, $S_2O_8^{2-}$ (16, 24), ferrate, FeO_4^{2-} (16, 25, 27), and peroxynitrite, $ONOO^-$ (26).

In this paper, we describe work designed to examine various oxidative leach-based pretreatment conditions and mimic plausible Waste Treatment Plant (WTP) plant operations for the selective removal of chromium from Hanford tank wastes from Tanks 241-SY-102 and 241-SX-101 (hereafter referred to as SY-102 and SX-101). It should be noted that much of the information presented here has been abstracted from previous reports (28, 29).

EXPERIMENTAL TESTING

This section provides details concerning the sludge samples from SY-102 and SX-101 used in this testing as well as the testing procedures and selected details concerning the data analysis employed.

Reagents and Equipment

All reagents used in this work were of analytical grade purity or higher. The hydroxide concentrations of stock solutions were verified by titration with primary standard acid solutions. Hydroxide concentrations in the leach

Table 1. Cr(III)/Cr(VI) compositions in Hanford Tank sludges before and after caustic leaching[a]

	Untreated sludge		% Cr Removed by dilute	After caustic leaching		% Removed		
Tank	Cr(III), %	Cr(VI), %	$[OH^-]$(wash)	Cr(III), %	Cr(VI), %	Total Cr	Cr(III)	Cr(VI)
B-111	73	27	27	>95	<5	41	18	>95
BX-107	91	9	21	>95	<5	29	22	>95
BY-110	69	31	47	>95	<5	48	2	>95
S-104	<5	>95	90	Not Detected		96	Not Detected	
S-107	89	11	24	>95	<5	53	38	>95
SX-108	13	87	71	>95	<5	78	24	>95
SY-103	>95	<5	5	>95	<5	13	13	>95
T-104	84	16	17	>95	<5	27	13	>95
T-111	78	22	24	>95	<5	64	54	>95

[a] Taken from reference 8.

solutions were measured by titration with standardized solutions of hydrochloric acid using a Mettler Model DL 21 Autotitrator.

Ultraviolet-visible (UV-vis) measurements were made on a 400-series charge-coupled device array spectrophotometer (Spectral Instruments Inc.) with a 200- to 950-nm scanning range. The solutions were held in PLASTIBRAND® 1-cm cuvettes. UV-vis spectroscopic measurements were obtained as follows: sample aliquots were diluted as necessary with 0.1 M NaOH, and the spectra from 350 to 800 nm were recorded on a Spectral Instrument's 400 series charged-coupled device (CCD) array UV-vis spectrophotometer. The chromate concentrations were determined by measuring the test solution's absorbance at 372 nm, which is the wavelength of maximum absorbance for chromate in the visible spectrum. The instrument was calibrated at this wavelength using standards-grade potassium dichromate in 1 M NaOH as described previously (30).

Samples for powder XRD measurements were prepared by slurrying a dried sludge sample with an amyl acetate-based, low X-ray background, glue, placing the slurry on a glass slide and drying the prepared sample before analysis. The XRD measurement was performed on a Sintag PAD V X-ray Powder diffractometer using Cu-Kα radiation and a solid-state detector. Measurement parameters include operation at 2 KW power, 0.02 degrees/step, and a 20 sec/step over a 2θ range of 5 to 65 degrees. The diffraction patterns were compared with known 2-theta/intensity data from the International Center for Diffraction Data (ICDD) database 49 (through 1999) to identify crystalline phases.

SEM-EDS measurements were performed using the model EDS2000 system with a 500 Digital processing unit and 5480 Imaging Interface (IXRF Systems Inc. Houston, Texas) connected to a 1610 scanning electron microscope (Amray Microscopes Inc. Bedford, Massachusetts). Samples of washed solids were fixed onto graphite tape and placed onto the SEM station stage, and the sample chamber was evacuated to 2E-07 to 4E-07 torr. The sample image then was brought into focus, and adjustments were made to the system's KV and spot size control. A digital image was captured on the computer screen, and subsections of that image were examined by x-ray microanalysis.

All gamma energy analysis (GEA), alpha energy analysis (AEA), and inductively coupled plasma-alpha energy analysis (ICP-AEA) measurements were performed with standard operations using in-house equipment.

Description of the SY-102 and SX-101 Sludge Samples

The SY-102 sample used for this testing is a composite of both liquid- and sludge-containing segments from two different core samples (Cores 284 and 286). Several glass bottles, whose contents ranged from primarily solids to mostly liquids, were prepared at the Hanford 222-S Laboratory and shipped to Battelle—Pacific Northwest Division (PNWD) in July 2003.

The SX-101 sample used for this testing is a composite of SX-101 sludge-containing segments from Core 225. Approximately 75 grams of this black slurry were prepared at the Hanford 222-S Laboratory and were shipped to PNWD in July 2003.

Initial Sludge Washing

For both the SY-102 and SX-101 samples, the shipped contents were mixed with a magnetic stirring bar, and a portion of each well-stirred suspension was transferred into a separate 50-ml centrifugation cone. The aliquots of the SY-102 and SX-101 samples individually were washed twice with enough 0.01 M NaOH so that the total volume of the suspension was 50 ml (an approximately 1 : 1 to 5 : 1 ratio [volume supernatant:volume centrifuge solids]). The solids were separated from the liquids by centrifugation after each wash and then were contacted repeatedly with fresh portions of 0.01 M NaOH at an initial solution-to-solids ratio of approximately 5 : 1. After each contact, the supernatant was decanted and discarded. These washings were repeated until the bulk of the color was removed (requiring typically 5 washes). Little color was observed in the final wash solution, although the yellow tinge imparted by the lead-glass windows of the hot cells where these manipulations were performed made detection of any yellow color imparted by the presence of alkaline Cr(VI) somewhat speculative. The final slurry was prepared by adding a portion of 0.01 M NaOH to the washed, centrifuged solids. For each sludge sample, two weighed aliquots of the well-stirred (using a Teflon®-coated magnetic stirring bar) suspension were removed and dried to a constant weight at 105°C. From this information, the amounts and concentrations of water-insoluble sludge were obtained

These dried samples were used for subsequent SEM, XRD, AEA, GEA, and inductively coupled plasma-auger electron spectroscopy (ICP-AES) measurements. Tables 2 and 3 summarize the concentrations of the major non-radioactive sludge components (defined here as $>10{,}000\,\mu g/g$ dried solids in either sludge) and the detected radionuclide components and concentrations.

Six aliquots were removed from the well-stirred sludge slurry, and each aliquot was transferred into a separate 30-ml plastic bottle. The reaction bottles then were transferred from the hot cells to a laboratory fume hood, and the reaction bottles were placed in a J-KEM heating/rotary aluminum shaker block into which holes, sized to securely hold the sample bottles, were cut. The depth of the holes kept the bulk of the test solution surrounded by the heating block. One position contained a blank solution of hydroxide into which a thermocouple was immersed. The thermocouple allowed the solution temperature to be maintained at temperature to within 1°C. Stock solutions of

Table 2. ICP-AES determined composition of major components in dilute hydroxide-washed SY-102 and SX-101 solids

Component	SY-102 Concentration, μg/g dried solids	SX-101 Concentration, μg/g dried solids
Al	171000	229000
Cr	73200	51500
Fe	59000	24800
Mn	14100	15600
Na	28100	25200
Si	14800	7300
U	7100	28000

the oxidant, 10 M NaOH, deionized water, and sodium permanganate solution were added as needed to meet the targeted experimental conditions.

Initial Caustic Leaching of Washed SY-102 and SX-101 Solids

The initial amount of settled solids was estimated as about 4 ml for both SY-102 and SX-101. An initial caustic leaching on samples SX-101-3, SX-101-4, SY-102-3, and SY-102-4 was performed. A volume of 3 : 1 leachate : settled solids (v : v) was targeted for a total target volume of 16 ml. To achieve 16 ml of an initial 3 M NaOH leach solution, 4.8 ml of 10 M NaOH and 8.2 ml DI water were added to each system. These bottles were loosely capped and heated for 8 hours at 85 ± 5°C. The heating was then stopped and the system cooled to room temperature overnight. The test suspensions then were centrifuged and the supernatants decanted into 30-ml plastic

Table 3. Concentrations of the major, identified radionuclides in dilute hydroxide-washed SY-102 and SX-101 solids

Component	SY-102 Concentration, μCi/g dried solids	SX-101 Concentration, μCi/g dried solids
^{239,240}Pu	3.71E + 01	1.28E + 00
^{243,244}Cm	7.18E − 02	8.89E − 02
^{238}Pu & ^{241}Am	1.29E + 02	4.52E + 00
Total α	1.66E + 02	5.89E + 00
^{137}Cs	7.10E + 01	4.86E + 01
^{60}Co	7.05E − 02	7.11E − 02
^{241}Am	1.36E + 02	5.19E + 00
^{154}Eu	2.17E + 00	2.97E + 00
^{155}Eu	1.10E + 00	1.46E + 00

vials. To the residual solids in each test container, 0.1 M NaOH was added at a 3 : 1 (v solution : v solids) ratio, the contents were mixed, the solids were again separated by centrifugation, and the solution was decanted into the sample container as the initial leachate solution. Washings were continued until the supernatant was colorless. Samples were then filtered through a 0.2-micron Nylon® syringe filter, and a 1-ml aliquot was placed in a container with 10 ml of 1 M nitric acid for ICP-AES analysis. A portion of the filtered leachate was stored in a 7-ml glass vial for further analysis.

Oxidative-Alkaline Leach Testing of SY-102 and SX-101 Solids

Table 4 summarizes the experimental conditions targeted for the oxidative-alkaline leaching tests.

After 24 hours of contact time, the test slurries were centrifuged (3000 rpm for a minimum of 5 minutes), and the supernatants were decanted from the residual solids. The residual solids were then washed three to four times with 0.1 M NaOH to remove any components present in the interstitial liquid. In all cases, the final wash solution appeared colorless. After each wash, the samples were centrifuged, and the supernatant was combined with the final leachate. A portion of the final leach solution was then filtered through a 0.2-μm Nylon® syringe filter, and a weighed aliquot of that filtered solution was added to a known amount of 1 M nitric acid to inhibit any precipitation before ICP-AES and radiochemical analysis.

Meanwhile, the 0.1 M NaOH-washed residual solids were dried to a constant weight at 105°C. These residual solids were subjected to a KOH fusion in a nickel crucible followed by dissolution into nitric acid. The content of the major metallic elements in both the acidified supernatants and dissolved residues was determined by ICP-AES for the initial washed solids. The radionuclide activities in both the acidified supernatants and dissolved residues were determined by alpha-energy analysis and gamma-energy analysis for the washed solids.

Table 4. Targeted experimental conditions for oxidative-alkaline leach testing

Sample number	Prior 3 M NaOH leach?	Post 3 M NaOH leach?	Oxidative leach $[NaOH]_{initial}$, M	Oxidative leach temp. °C	Oxidative Leach $[NaMnO_4]_{initial}/[Cr]$
Tank#-1	No	No	3	85	1.1
Tank#-2	No	No	5	85	5
Tank#-3	Yes	No	0.25	25	1.1
Tank#-4	Yes	No	0.25	85	1.1
Tank#-5	No	Yes	0.25	85	1.1

Final Caustic Leaching of Washed SY-102 and SX-101 Solids

Following the oxidative-alkaline leaching and washing of the leached solids, a final 3 M NaOH leach was performed on samples SX-101-5, and SY-102-5, as described previously for samples SX-101-3, SX-101-4, SY-102-3, and SY-102-4.

Estimation of the Glass Volumes Required to Immobilize Pretreated Sludge

The impact of various leaching techniques on glass volume was estimated using a systematic method that optimized waste loading in glass. A set of conditions, consistent with current RPP-WTP vitrification process and compliance strategies, were met simultaneously. The glass-forming chemical concentrations were varied until the waste loading was a maximum while meeting the full set of conditions. This approach has been described in full previously (27–29).

To evaluate the overall impact on IHLW of each leach test, the key information needed is the metal concentrations of the leached solids together with the mass changes that occurred as a result of leaching or alternatively, the mass of each component present after a leach step. To evaluate the impact of an intermediate leach step, the necessary data were not directly available. However, this information could be obtained indirectly as follows: first, the sample mass of each component present after an intermediate leach step is calculated by taking the initial mass and subtracting the mass removed by the intermediate step. The mass of each metal component as its stable oxide is then calculated, and the masses of these oxides are summed to give the total oxide concentration. This calculation of the sample mass following a leach and dilute hydroxide wash assumes that 1) the metals are present as these oxides, 2) there are no other anions present, such as chloride, fluorides, or nitrates, and 3) the metals not available by ICP-AES analysis of the solutions and leached residual solids (such as Ni and K because of the interferences from the KOH fusion in a Ni crucible used to prepared the leached solids for analysis) are not present in significant concentrations.

RESULTS AND DISCUSSION

This section discusses the analyses of washed SY-102 and SX-101 sludge solids with various techniques. It also discusses oxidative leach testing, the dissolution of non-radioactive and radioactive components, and the glass volumes resulting from immobilization of SX-101 and SY-102 sludge as a function of oxidative-alkaline leaching.

ICP-AES and Radiochemical Analysis of Washed SY-102 and SX-101 Sludge Solids

As described in the experimental section, the sludges were washed repeatedly with 0.01 M NaOH. This washing process removed all readily soluble chromium from the sludge, allowing the testing to focus on removing the dilute hydroxide-insoluble chromium. After each contact, the wash solution was separated from the solids by centrifugation. At least five contacts, each at about a 5 : 1 solution-to-solids volume, were performed, after which it was assumed, based on previous experience, that the bulk of the water-soluble components had been removed from the interstitial liquid in the sludges. The residual solids were then suspended in dilute NaOH, and aliquots were taken for analysis.

Samples of the washed solids were dissolved by KOH fusion followed by nitric acid dissolution. The metals composition was determined by ICP-AES, and the radionuclide content was evaluated by AEA and GEA. Table 2 shows the concentrations of the major bulk components in the washed sludges. For both SX-101 and SY-102, aluminum is the primary metal present, followed by chromium. Substantial amounts of iron, sodium, manganese, and silicon (for SY-102) were also detected. The uranium content of the washed SX-101 solids was about a factor of four higher than that for the washed SY-102 solids.

Table 3 summarizes the major radionuclide contents of the two washed sludges. Overall, the radionuclide concentrations in the washed sludges are similar: however, there is an order-of-magnitude greater plutonium and two orders of magnitude greater americium concentration in the washed SY-102 sludge than in the washed SX-101 sludge.

Analysis of the SY-102 and SX-101 Solids by XRD

The distribution and composition of the major sludge components were explored by X-ray powder diffraction to identify any crystalline phases and SEM/EDS to evaluate the distribution of the dominant metals present in the washed sludges. For both sludges, the only crystalline material present is gibbsite, $Al(OH)_3$. For SX-101, a second phase was also identified, that of the uranium(VI) mineral, clarkeite, $Na[UO_2(O)(OH)]$. The presence of detectable quantities of a uranium-containing mineral in the washed SX-101 sludge is consistent with the greater concentrations of uranium found in that sludge.

SEM/EDS Analysis of the SY-102 and SX-101 Solids

SY-102 Washed Solids

The SEM-EDS analysis of washed SX-101 and SY-102 sludge solids reveals information about the distribution of the major metals in the sludge.

The majority of the particles found in the small SY-102 sludge samples examined were similar in size and shape and can be described as irregularly shaped solids with a "spongy" texture. A second type of particle was observed in the SY-102 washed solids. This particle appears to have a much better defined shape, and the EDS analysis indicates aluminum to be the primary metallic element present. The particle is likely that of the crystalline gibbsite revealed to be present by the XRD analysis.

The SEM analysis of SY-102 solids indicates that aluminum, iron, and chromium tend to be uniformly distributed in the bulk of the solids, with the exception of crystalline particles containing solely gibbsite. The presence of aluminum as gibbsite bodes well for the success of alkaline leaching at removing the bulk of the aluminum from the tank sludge.

SX-101 Washed Solids

One major type of sludge particle was observed by SEM. As with the SY-102 particle, the major observed components chromium, manganese, and iron seem to be broadly and evenly distributed throughout the particle. Aluminum, silica, and sodium are evenly distributed throughout much of the particle. Finally, a broad view revealed some small irregular solids composed mostly of aluminum. Because of the irregular shape of this particle, some sort of amorphous $Al(OH)_3$ is postulated for its composition. No pure uranium crystalline phases were found, despite the identification of clarkeite by XRD.

Oxidative Leach Testing—Experimental Design and Execution

The conditions for oxidative-alkaline leach testing were chosen to focus on three process variables: temperature, hydroxide concentration, and the order of alkaline leaching processes. In all cases, the initial solids volume to total leachate volume was kept constant at 1 : 4 (1 part settled sludge volume and three parts added solution volume). Tests 1 and 2 explore the possibility of combining a high hydroxide, high temperature, leach for aluminum removal with concomitant permanganate addition for chromium removal. Test 1 uses the standard caustic-leaching conditions (3 M NaOH, 85°C) whereas Test 2 explores the impact of a potential upset condition of excess permanganate and hydroxide at elevated temperature.

Tests 3 through 5 explore the impact of temperature and the order of alkaline leach operations. In all cases, the targeted oxidative-alkaline leach conditions employ a targeted slight stoichiometric excess of permanganate and a low (0.25 M) initial hydroxide concentration in the leachate. Within the groups of tests (3 and 4), the variable is that of temperature (ambient temperature, 25°C, or elevated temperature, 85°C). The order of leaching was examined between Tests 3 and 4 and in Test 5. For Tests 3 and 4, a caustic leach was performed before oxidative leaching, and for Tests 5, a standard caustic leach was performed following oxidative-alkaline leaching.

A comparison of temperature variation for Test 5 was performed similar to that for tests 3 and 4. However, because of analytical difficulties, interpretation of the results is difficult and will not be discussed in this paper.

In previous oxidative-alkaline leach tests examining the effect of free hydroxide concentration, the lower initial hydroxide concentrations were typically less than that targeted in this test. The reason for this difference lies in the lower leachate-to-solids ratio in these tests compared to those previously. However, both the reaction of permanganate with Cr(III) hydroxide to form manganese dioxide and chromate and the dissolution of aluminum oxide consume hydroxide. Indeed, the low hydroxide concentration experiments possess only enough free hydroxide for the chromium reaction to go to completion whereas the high hydroxide tests possess enough hydroxide to oxidize chromium and dissolve aluminum. For tests with separate caustic leaches associated with the low hydroxide oxidative leach, enough hydroxide is supplied in the caustic leach step to dissolve all aluminum not consumed by the oxidative-alkaline leach treatment.

For the 25°C tests, the presence of permanganate/manganate could still be seen visually after 2 hours. For the 85°C oxidative leach tests, after 2 hours, all visual signs of permanganate had disappeared, with the exception of Test SX-101-5. For the samples with no visual presence of permanganate, 0.5 ml (approximately 0.1 to 0.2 equivalents additional permanganate) was added. After 6 hours, all of the SY-102 leachates and the SX-101-2 leachate showed no visual signs of permanganate; at this point, another 0.5 ml of 0.5 M sodium permanganate solution was added to these leachate solutions. After 24 hours of contact time, only the SX-101-5 test showed visual indications of the presence of permanganate in solution.

Dissolution of Non-Radioactive Components

Table 5 summarizes the overall removal of the major non-radioactive components present in the washed SX-101 and SY-102 solids as a function of the differing oxidative-alkaline leach methods tested.

Component removals were calculated by summing the total mass of each component found in all leach solutions together with the mass of the component in the residual solids and calculating the fraction of mass removed in the leachate from the calculated total mass.

As expected, the oxidative-alkaline leaching primarily dissolves both aluminum and chromium. Generally, aluminum removals are good to excellent ($>80\%$, often $>90\%$). Generally, removal of chromium also is high, but the dependence of chromium removals varies more with the leach conditions, ranging from $>50\%$ to $>95\%$. Test condition #2 (5 M NaOH, excess permanganate, 85°C) is markedly less effective at chromium removal.

Table 5. Overall major component removal from SX-101 and SY-102 washed-sludges by oxidative-alkaline leaching

	% Component removal					
Test #	Al	Cr	Fe	Mn	Si	U
SX-101-1	96	96	<0.1	0	42	0
SX-101-2	96	66	0.3	0	43	0
SX-101-3	83	87	0.3	0	46	0
SX-101-4	89	94	0.3	0	50	0
SX-101-5	97	97	0.3	0.2	67	0
SY-102-1	86	94	<0.1	0	17	0
SY-102-2	88	46	<0.1	0	22	0
SY-102-3	76	80	0.1	63	32	0
SY-102-4	78	95	0.2	0	36	0
SY-102-5	89	96	<0.1	0	28	0

The major components removed in this process were Al and Cr. However, the steps at which such removal occurs varied distinctly, as shown in Table 6.

As expected with these 8-hour contact times, little Cr is removed by simple caustic leaching, with the bulk of the Cr being removed by oxidative alkaline leaching. Consistent with the rapid kinetic dissolution of identified Al-containing phases such as gibbsite (31) in these washed sludges, if the initial leach is performed at high initial free hydroxide, the majority of the dissolved Al occurs during the initial leach. The slight additional amounts of dissolved Al found in subsequent oxidative alkaline leaching could be caused by several factors. For example, some of the Al could be incorporated into primarily Cr-containing phases and so not be in contact with the leachate solution until the extensive Cr removal found for oxidative alkaline leaching occurs. Alternatively, some material could have reprecipitated from a

Table 6. Summary of al and cr leach behavior with SX-101 and SY-102 washed sludges

	% Removed					
Test	Cr CL[a]	Cr OL	Cr Total	Al CL	Al OL	Al Total
SX-101-3	6	82	87	79	4	83
SX-101-4	5	89	94	79	10	89
SX-101-5	94	3	97	14	83	97
SY-102-3	4	76	80	72	5	76
SY-102-4	4	91	95	69	9	78
SY-102-5	90	6	96	5	84	89

[a] CL = 3 M NaOH caustic leach; OL = oxidative leach.

supersaturated leachate solution or have reprecipitated from the interstitial liquid when the hydroxide and ionic strength are dropped precipitously by contact with a wash solution.

Significant amounts of Si are removed during leaching, but the amount appears to be independent of the leach conditions (but not the sludge type). Minor amounts of iron are removed, and the fractions removed appear to be independent of both the leach conditions and sludge type.

Chromium Dissolution and Chromate Formation

All oxidative leach solutions and subsequent washes were analyzed both by ICP-AES for the total chromium concentrations and by spectrophotometry for the chromate concentrations. In addition, the prior and subsequent 3 M NaOH/85°C leach and washes were analyzed in this manner as well. Overall, the agreement between total chromium and chromate measurements is excellent, well within the 15% uncertainty claimed for the ICP-AES measurements of chromium. An exception is noted: the SY-102-5 final leachate solution is the only solution that appears to have slightly more total chromium than chromate. No Cr(III) was detected by spectrophotometry, but the low extinction coefficients for Cr(III) compared to Cr(VI) indicate that such a low Cr(III) concentration suggested by the difference would be below detection limits.

Radionuclide Dissolution

One concern about employing oxidative-alkaline leaching is that concomitant oxidation of plutonium to Pu(VI) would lead to a problematic enhanced dissolution of plutonium. To evaluate this possibility, the radionuclide content of the leachate and wash solutions was measured by GEA and AEA to determine the extent of radionuclide dissolution, in particular actinide dissolution. Table 7 shows the results.

The results for both the SY-102 and SX-101 sludges show similar trends. The only radionuclides that show any significant dissolution are plutonium and Cs. The Cs dissolution tends to be fairly constant at around 30 to 40% dissolution regardless of the sludge type or reaction conditions.

With respect to plutonium dissolution, adding permanganate to a standard caustic-leach solution (i.e., condition number 1) results in the most enhanced plutonium dissolution of all the leach conditions tested. Interestingly, increasing the initial hydroxide concentration still further, from 3 to 5 M, in the presence of a greater excess of permanganate, causes a drop in the amount of plutonium dissolved. Performing a standard caustic leach following permanganate addition (i.e., condition 5) results in more plutonium dissolution than reversing the order and performing an initial caustic leach followed by

Table 7. Radionuclide removals from SX-101 and SY-102 washed sludges by oxidative-alkaline leaching

	%Component removal						
Test	^{239,240}Pu	^{241}Am	^{243,244}Cm	Total α	^{60}Co	^{137}Cs	^{154}Eu
SX-101-1	13	<0.01	<0.01	3.2	<0.01	27	<0.01
SX-101-2	<0.1	<0.01	<0.01	<0.1	<0.01	33	<0.01
SX-101-3	<0.1	<0.01	<0.01	<0.1	<0.01	33[a]	<0.01
SX-101-4	<0.1	<0.01	<0.01	<0.1	<0.01	33[a]	<0.01
SX-101-5	2.8[a]	<0.01	<0.01	0.7[a]	<0.01	29	<0.01
SY-102-1	0.6	<0.01	<0.01	0.1	<0.01	22	<0.01
SY-102-2	<0.1	<0.01	<0.01	<0.1	<0.01	37	<0.01
SY-102-3	<0.1	<0.01	<0.01	<0.1	<0.01	40[a]	<0.01
SY-102-4	<0.1	<0.01	<0.01	<0.1	<0.01	41[a]	<0.01
SY-102-5	0.2[a]	<0.01	<0.01	<0.1[a]	<0.01	37	<0.01

[a] Component fraction removed during 3 M NaOH caustic leach greater than that removed during oxidative-alkaline leaching.

a low hydroxide oxidative leach (i.e., conditions 3 and 4). Notably, in this case (condition 5), the bulk of the plutonium dissolution is found during the subsequent caustic leach and not during the oxidative leach. The reasons for this are unclear, but perhaps it is a kinetic effect: additional plutonium dissolves during oxidative leaching but reprecipitates during cooling/washing. This freshly reprecipitated plutonium then more rapidly redissolves during the relatively short 8-hour contact times of the standard caustic leach. Finally, performing the oxidative leach at 85°C (conditions 4 and 5) results in a small enhancement in plutonium dissolution compared to performing a 25°C oxidative leach (condition 3). In almost all cases, though, the extent of plutonium dissolution is relatively minor, especially when compared to the extent of aluminum and chromium removal described above.

Glass Volumes or Immobilization of SX-101 and SY-102 Sludge as a Function of Oxidative-Alkaline Leaching

The ultimate goal of oxidative-alkaline leaching is to reduce the amount of IHLW produced while producing a leachate that can be made into acceptable immobilized low-activity waste (ILAW). In this section, we attempt to evaluate how effective the various test conditions were at achieving that goal. To evaluate the effectiveness of various leach conditions, we calculated the amount of glass required to immobilize one arbitrary unit of treated sludge. Three sets of loadings were calculated, one based on the DOE's minimum contract requirements (TS-1.1 in Table 8), one using the current WTP baseline model for IHLW, and one using an expanded model with a relaxed restriction on chromium concentration. Table 8 summarizes the results of the IHLW calculations as well as providing the limiting constituent to immobilizing the treated sludge.

The mass changes between the initial washed sludge used for testing and the actual metals content as determined by ICP-AES of the treated solids were used in the calculations summarized in Table 8. However, no test was performed only looking at the impact of a standard caustic leach; therefore, evaluating the loading of only a caustic leach required a different approach. The total amount of each component was obtained from the data in tests-3 and -4 where an initial 3 M NaOH/85°C caustic leach was performed. This was calculated from the initial estimate of sludge used in the test multiplied by the metals concentration in the washed sludge solids. The total mass of each metal component removed during caustic leaching was determined by the total volume of leachate multiplied by each metal component's concentration in the leachate. The total amount in the leachate was subtracted from the total amount initially present to give the total amount of each component in the caustic-leached solids. These values were then converted to metal oxide wt%, assuming only that the measured metal oxides were present in the caustic-leached solids, and these amounts were normalized to one gram of initial washed sludge. The resulting weight percent metal oxides then were used in the IHLW calculations.

Note that despite the very high aluminum concentrations (see Table 2) present in the washed SY-102 and SX-101 sludges, chromium remains the limiting component to sludge loading in IHLW. Performing a simple caustic leach yields little (SX-101) to a modest (SY-102) reduction in the amount of IHLW produced. The calculations actually show an increase in the amount of IHLW produced if just a caustic leach is performed; we believe this to be an artifact of the indirect approach taken to obtain the composition of a caustic-leached sludge. The condition of 5 M NaOH/excess permanganate provides relatively poor removal of chromium and is the least effective condition for reducing the amount of IHLW. The most effective conditions are where the oxidative-alkaline leach is performed at 85°C (Tests-1, -4, and -5), where greater than an order of magnitude reduction in IHLW is predicted. Indeed, in these cases, manganese now replaces chromium as the limiting component in the amount of sludge loaded into IHLW.

Examination of the consequences of the individual process steps present in test conditions 3 through 5 yield similar insights. Unlike the response to an initial caustic leach, performing an initial oxidative leach reaps the bulk of the benefits for reducing the amount of IHLW. In the optimum sequence of an initial 85°C oxidative leach, almost an order of magnitude reduction in IHLW can be achieved, and the limiting condition shifts from Cr to Al or, in selected cases, to a glass property constraint. Even in the 25°C oxidative leach, the oxidative leach is effective at removing Cr as the

Table 8. Calculated effectiveness of oxidative-alkaline leaching on IHLW volumes

	Units of glass produced/unit treated sludge (waste limiting component/condition)		
	TS-1.1	Current	Expanded
SX-101 washed	15.0($Cr_2O_3 = 0.5$)	15.0($Cr_2O_3 = 0.5$)	7.5($Cr_2O_3 = 1.0$)
SX-101-1 total	0.6($Cr_2O_3 = 0.5$)	1.6($MnO = 7.0$)	1.6($MnO = 7.0$)
SX-101-2 total	5.3($Cr_2O_3 = 0.5$)	5.3($Cr_2O_3 = 0.5$)	2.7($Cr_2O_3 = 1.0$)
SX-101-3 caustic leached only	14.7($Cr_2O_3 = 0.5$)	14.7($Cr_2O_3 = 0.5$)	7.3($Cr_2O_3 = 1.0$)
SX-101-3 total	2.0($Cr_2O_3 = 0.5$)	2.0($Cr_2O_3 = 0.5$)	1.2($MnO = 7.0$)
SX-101-4 caustic leached only	14.4($Cr_2O_3 = 0.5$)	14.4($Cr_2O_3 = 0.5$)	7.2($Cr_2O_3 = 1.0$)
SX-101-4 total	0.9($Cr_2O_3 = 0.5$)	1.3($MnO = 7.0$)	1.3($MnO = 7.0$)
SX-101-5 ox leached only	2.0($Al_2O_3 = 11$)	2.6($Al_2O_3 = 8.5$)	1.5($Al_2O_3 = 15$)
SX-101-5 total	0.3($Cr_2O_3 = 0.5$)	1.1($MnO = 7.0$)	1.1($MnO = 7.0$)
SY-102 washed	21.3($Cr_2O_3 = 0.5$)	21.3($Cr_2O_3 = 0.5$)	10.7($Cr_2O_3 = 1.0$)
SY-102-1 total	1.1($Cr_2O_3 = 0.5$)	1.9($MnO = 7.0$)	1.9($MnO = 7.0$)
SY-102-2 total	13.0($Cr_2O_3 = 0.5$)	13.0($Cr_2O_3 = 0.5$)	6.5($Cr_2O_3 = 1.0$)
SY-102-3 caustic leached only	23.7($Cr_2O_3 = 0.5$)	23.7($Cr_2O_3 = 0.5$)	11.8($Cr_2O_3 = 1.0$)
SY-102-3 total	4.9($Cr_2O_3 = 0.5$)	4.9($Cr_2O_3 = 0.5$)	2.5($Cr_2O_3 = 1.0$)
SY-102-4 caustic leached only	25.3($Cr_2O_3 = 0.5$)	25.3($Cr_2O_3 = 0.5$)	12.6($Cr_2O_3 = 1.0$)
SY-102-4 total	1.3($Cr_2O_3 = 0.5$)	2.0($MnO = 7.0$)	2.0($MnO = 7.0$)
SY-102-5 ox leached only	2.8($Al_2O_3 = 11$)	3.7($Al_2O_3 = 8.5$)	2.2(T1% = 950)[a]
SY-102-5 total	0.9($Cr_2O_3 = 0.5$)	2.1($MnO = 7.0$)	2.1($MnO = 7.0$)

TS-1.1 = contract minimum loadings.

Current = WTP baseline.

Expanded = using an expanded region of validity for glass properties models.

[a] Temperature at which the equilibrium volume in glass is 1% (on a quenched glass basis).

limiting component in most of the IHLW loading conditions examined. In short, despite that large amount of sludge mass that is removed from the sludge solids and transferred to the LAW stream by either an initial oxidative leach or an initial caustic leach, it appears that little to no decrease in the amount of IHLW will result from performing a simple caustic leach on washed SX-101 and SY-102 sludge solids. Rather, an initial oxidative leach will reap most of the benefits observed by a sequential oxidative alkaline leach and caustic leach no matter what the order of the leach sequence.

SUMMARY AND CONCLUSIONS

The focus of the work described in this report was to evaluate various alternative conditions for the selective removal of chromium through oxidative-alkaline leaching with permanganate. The test conditions, unlike prior studies, were performed under leach conditions more closely resembling those likely to be used at the WTP.

Five conditions are described. The first leach condition involved contact of washed SX-101 and SY-102 tank solids with a slight stoichiometric excess of permanganate using the standard caustic-leach conditions of initial 3 M NaOH and a leach temperature of 85°C. The second leach condition involved contact of washed SX-101 and SY-102 tank solids with excess initial hydroxide (5 M) and excess permanganate. The third leach condition involved contact of washed SX-101 and SY-102 tank solids with an initial standard caustic leach followed by contact with a slight stoichiometric excess of permanganate at lower initial hydroxide concentration (0.25 M) at 25°C. The fourth leach condition was similar to the third leach condition except that the oxidative leaching step was conducted at 85°C. A fifth leach condition involved contact of washed SX-101 and SY-102 tank solids initially with permanganate at lower initial hydroxide concentration (0.25 M) at 85°C, followed by treatment with the standard caustic-leach conditions of 3 M NaOH and 85°C. These leach tests were performed at a targeted 3 : 1 volume of leachate-to-volume of settled tank solids.

Various analyses were performed to evaluate the leaching process. The initial solids were examined for selected metals content by ICP-AES, for TRU elements by AEA, and for gamma-emitting isotopes by GEA. The distribution of the major bulk components within individual solid particles was evaluated by SEM/EDS, and crystalline phases present were evaluated by XRD.

For both the SX-101 and SY-102 washed solids, the major crystalline phase observed was gibbsite, $Al(OH)_3$. For SX-101, an uranium-containing phase, clarkeite, $Na[(UO_2)(O)(OH)]$, was also observed. SEM-EDS analysis indicated that, with the exception of these phases, the major non-radioactive tank components tended to be evenly distributed throughout the solids, although some exceptions were noted.

In general, effective removal of chromium and aluminum was observed, with relatively little plutonium dissolution. Surprisingly, under the most extreme conditions of hydroxide, permanganate, and temperature, less effective aluminum, chromium, and plutonium removal is observed with respect to most of the other leach conditions.

Consistent with some earlier reports, adding permanganate under the standard caustic-leach conditions results in some enhancement in the fraction of dissolved plutonium. No significant amounts of any other TRU elements were detected in the leach solutions. Performing the oxidative leach at 85°C generally results in a slight enhancement of aluminum and chromium dissolution with little enhancement in dissolved plutonium.

A comparison of dissolved chromate to total chromium dissolved indicates, consistent with prior reports, that the bulk of the dissolved chromium is present as chromate.

Overall, testing indicates that effective removal of aluminum and chromium is possible, with greater than 95% removals achievable. In previous washed sludges with large quantities of chromium, SEM-EDS analysis has indicated that the chromium is generally present either in a pure chromium oxide phase or together with aluminum, another element generally well removed by caustic leaching. However, with SX-101 and SY-102, substantial iron and manganese appears to be mixed with the leachable metals aluminum and chromium. Despite the possibility then that chromium removal might be inhibited by the presence of these unleachable metals passivating the particle surface and making the chromium in the bulk of the sample inaccessible to oxidant, excellent removal of chromium was observed. Unfortunately, a SEM-EDS examination of the leached solids was not performed.

An analysis of the waste-oxide loading of the washed sludges indicates that greater than an order of magnitude increases in waste-oxide loading are possible following oxidative-alkaline leaching for both the washed SX-101 and SY-102 tank solids. The analysis also suggests that a simple caustic leach (under the baseline WTP conditions) is much less effective at increasing waste-oxide loadings in IHLW and that performing oxidative-alkaline leaching, under several of the tested leach conditions, can remove chromium as the waste-oxide limiting component.

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